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### Citation for published version:

Gilfillan, S, Sherk, GW, Poreda, RJ & Haszeldine, R 2017, 'Using noble gas fingerprints at the Kerr Farm to assess CO<sub>2</sub> leakage allegations linked to the Weyburn-Midale CO<sub>2</sub> Monitoring and Storage Project', *International Journal of Greenhouse Gas Control*, vol. 63, pp. 215-225.  
<https://doi.org/10.1016/j.ijggc.2017.05.015>

### Digital Object Identifier (DOI):

[10.1016/j.ijggc.2017.05.015](https://doi.org/10.1016/j.ijggc.2017.05.015)

### Link:

[Link to publication record in Edinburgh Research Explorer](#)

### Document Version:

Peer reviewed version

### Published In:

International Journal of Greenhouse Gas Control

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# Using noble gas fingerprints at the Kerr Farm to assess CO<sub>2</sub> leakage allegations linked to the Weyburn-Midale CO<sub>2</sub> Monitoring and Storage Project

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**Keywords:** Carbon storage, Kerr Farm, Weyburn-Midale, Noble gases, Carbon isotopes, Groundwater monitoring

## Abstract

For carbon capture and storage technology to successfully contribute to climate mitigation efforts, the stored CO<sub>2</sub> must be securely isolated from the atmosphere and oceans. Hence, there is a need to establish and verify monitoring techniques that can detect unplanned migration of injected CO<sub>2</sub> from a storage site to the near surface. Noble gases are sensitive tracers of crustal fluid input in the subsurface due to their low concentrations and unreactive nature. Several studies have identified their potential to act as tracers of deep fluid migration to the shallow subsurface, but they have yet to be used in a contested situation. In January 2011 it was reported extensively in global media that high CO<sub>2</sub> concentrations in soils and related groundwater pollution had been identified on a farm property belonging to the Kerr family, located near to the town of Weyburn in Saskatchewan, Canada. The origin of this CO<sub>2</sub> pollution was cited to be the nearby Weyburn-Midale CO<sub>2</sub> Monitoring and Storage Project. Here, as part of an investigation funded independently of the Weyburn-Midale field operators, we present  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $^3\text{He}/^4\text{He}$ ,  $^4\text{He}/^{20}\text{Ne}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$  and Kr measured in waters obtained from four groundwater wells located on and surrounding the Kerr property. We aim to establish if stable carbon and noble gas natural tracers are effective at determining if migration of CO<sub>2</sub> from the storage project was responsible for the alleged high CO<sub>2</sub> concentrations and water pollution measured on the Kerr farm. We compare the stable carbon isotope and noble gas 'fingerprints' of the Kerr groundwaters to those expected in a water equilibrated with the

atmosphere under local recharge conditions, the produced CO<sub>2</sub> obtained from production wells, and the CO<sub>2</sub> injected into the Weyburn and Midale oil fields. We find that the stable carbon isotope data do not constrain the origin of the dissolved CO<sub>2</sub> in the Kerr groundwaters. Due to low noble gas concentrations in the captured CO<sub>2</sub> we are unable to completely rule out the presence of 20 to 34% contribution from injected CO<sub>2</sub> to the groundwaters surrounding the Kerr property. However, we find that all of the Kerr groundwater samples exhibit noble gas fingerprints that would be expected in a shallow groundwater in contact with the atmosphere and hence there is no evidence for the addition of a deep radiogenic component or dilution from the addition of a gas phase low in atmospheric derived noble gases. Our findings corroborate previous studies that indicate that elevated CO<sub>2</sub> concentrations found on the Kerr property are almost certainly of biological origin, and not migrated from the deep subsurface. The comprehensive follow up to these CO<sub>2</sub> leakage allegations outlined in this study provides a robust framework for responses to any future leakage allegations at CO<sub>2</sub> storage sites and further highlights that no single technique can categorically identify the origin of CO<sub>2</sub> in the shallow subsurface. Hence, it is essential that the full range of geochemical tracers (stable carbon and <sup>14</sup>C isotopes, noble gases, water chemistry, process based gas ratios) are integrated with a comprehensive understanding of geological and engineering data in response to CO<sub>2</sub> leakage allegations in the future.

## **1. Introduction**

For Carbon Capture and Storage (CCS) technology to be routinely deployed evidence is required that large volumes of CO<sub>2</sub> can be injected into the subsurface and securely retained. This evidence base can only be provided through evaluation of the containment performance of both natural CO<sub>2</sub> reservoirs (Miocic et al., 2013; Miocic et al., 2016) and through the evaluation of the security of engineered CO<sub>2</sub> storage sites (Wolaver et al., 2013). Around the world several large scale CO<sub>2</sub> injection projects have been initiated to provide this evidence base. The largest of these is operating at the Weyburn and Midale oil fields in Saskatchewan, Canada, where CO<sub>2</sub> has been introduced into the Weyburn field since 2000, and the Midale field since 2005, to both increase oil recovery, termed CO<sub>2</sub>-enhanced oil recovery (EOR), and for storage purposes (Whittaker et al., 2011). The injected CO<sub>2</sub> is sourced from the Dakota Gasification plant in North Dakota and is pumped some 320 km to the oil fields, and ~20 Mt of CO<sub>2</sub> had been injected by the start of 2011 (Whittaker et al., 2011). Currently, 2.4 Mt/year and 0.4 Mt/year of CO<sub>2</sub> are injected into the Weyburn and Midale oil fields, respectively, and it is intended that in excess of 40 Mt of CO<sub>2</sub> will be stored in the fields in total (IEA Greenhouse Gas Programme, 2004).

There are many natural sources of CO<sub>2</sub> within the crust with overlapping geochemical signatures, including breakdown of carbonate minerals or cements, biological activity or hydrocarbon oxidation (Romanak et al., 2014; Wycherley et al., 1999). This makes it extremely difficult to unequivocally detect the small releases of anthropogenic CO<sub>2</sub> that could arise from a diffuse leakage of CO<sub>2</sub> from a storage site. Hence, there is a need to establish and verify monitoring techniques that can detect any unplanned migration of CO<sub>2</sub> from a storage site to the near surface. The requirement for such leakage assessment techniques was clearly demonstrated in January 2011, when landowners living near the International Energy Agency Greenhouse Gas (IEAGHG) Weyburn–Midale CO<sub>2</sub> Monitoring and Storage Project in Saskatchewan, Canada, announced to international media that CO<sub>2</sub> was leaking into the soil and groundwater on their property.

These allegations were based on a soil gas study undertaken over the property in the summer of 2010 by a geochemical consultancy, Petro-Find GeoChem Ltd. This study found that soil gas CO<sub>2</sub> concentrations averaged ~2.3%, and recorded a soil gas anomaly of ~11% measured in the northern portion of the property (Lafleur, 2010). Petro-Find attributed the source of this soil gas anomaly to the CO<sub>2</sub> injected into the nearby Weyburn-Midale CO<sub>2</sub>-EOR field based on the measured range of stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of soil gas being between -21.6 and -22.9‰, similar to the  $-20.4 \pm 0.4\text{‰}$  values of the CO<sub>2</sub> injected into the EOR reservoir (Lafleur, 2010).

The Petroleum Technology Research Centre (PTRC), which is responsible for the environmental monitoring of the CO<sub>2</sub> storage project, immediately published a science based response refuting the allegations. This stated that Petro-Find had not taken into account similar soil gas  $\delta^{13}\text{C}$  (CO<sub>2</sub>) values observed in prairie soils comparable to those on the Kerr property measured on a control site some distance away from the CO<sub>2</sub>-EOR field (Rubin and Zhai, 2012), and that there are several other natural sources that could account for the measured  $\delta^{13}\text{C}$  (CO<sub>2</sub>) values (NETL, 2010; Petroleum Technology Research Centre, 2011). Whilst this went some way to addressing the public fears that the CO<sub>2</sub> leakage allegations raised, there was a clear need for both the fledgling CO<sub>2</sub> storage industry and the local community to have the allegations independently investigated in order to establish if there was any validity to them.

Following the allegations, three separately funded, and independently conducted investigations were launched. The first of these was undertaken by European scientists who had completed 10 years of near-surface monitoring at the nearby Weyburn-Midale CO<sub>2</sub> EOR field (Beaubien et al., 2013). A second study was commissioned by the Weyburn field operators, Cenovus Energy Inc. (Cenovus), and undertaken by three third parties external to

Cenovus; TRIUM Environmental, Chemistry Matters and TERA Environmental Consultants. Once completed, the TRIUM Environmental and Chemistry Matters site investigation was then independently reviewed by the PTRC. A third study was co-ordinated by the International Performance Assessment Centre for Geological Storage of CO<sub>2</sub> (IPAC-CO<sub>2</sub>), a not-for-profit research and development organisation founded in 2008. IPAC-CO<sub>2</sub> was established to fill a gap in the understanding and assessment of risk and performance in the Carbon Capture and Storage chain by providing independent, objective information, best practices, advice and assessments to governments and industry (ZeroCO2.no, Accessed 1st March 2016). IPAC-CO<sub>2</sub> was funded by Royal Dutch Shell and the Government of Saskatchewan, and hosted at the University of Regina (Saskatchewan, Canada). Prior to the Kerr allegations, IPAC-CO<sub>2</sub> developed an Incident Response Protocol (IRP) that would be implemented if there were allegations of CO<sub>2</sub> leakage at a CCS project (Sherk, 2011). This IRP provided a framework and foundation for the Kerr investigation which comprised three distinct activities undertaken on the Kerr property and surrounding area; (i) chemical analysis of soil gases (Romanak et al., 2014), (ii) stable C isotope and noble gas analysis of the shallow groundwaters (this study), (iii) hydrogeological analysis (Wolaver et al., 2011).

Here, we present measurements of the  $\delta^{13}\text{C}$  values of DIC and noble gas measurements (<sup>3</sup>He/<sup>4</sup>He, <sup>4</sup>He/<sup>20</sup>Ne, Ne, Ar and Kr) from waters obtained from four groundwater wells located on and surrounding the Kerr property. We compare these measurements to the geochemical fingerprints expected in a water equilibrated with the atmosphere and those measured in the injected CO<sub>2</sub> and fluids produced from the Weyburn CO<sub>2</sub>-EOR reservoir. We use this comparison to assess the role that inherent stable C isotopes and noble gas fingerprints can play in evaluating the validity of the allegations of leakage on the Kerr property.

## **2. Investigation Background**

### *2.1. Scientific Background*

$\delta^{13}\text{C}_{\text{DIC}}$  measurements have been extensively used in tracing CO<sub>2</sub> injected into the Weyburn field and other CO<sub>2</sub> storage test sites (Johnson et al., 2009; Raistrick et al., 2006). They have proved to be effective at tracking the migration and fate of CO<sub>2</sub> injected into the Weyburn-Midale field (Mayer et al., 2013) and at several shallow CO<sub>2</sub> leakage monitoring pilot projects (Jones et al., 2015; McAlexander et al., 2011; Moni and Rasse, 2014; Schulz et al., 2012). However, the effectiveness of  $\delta^{13}\text{C}_{\text{DIC}}$  as a sole means to track the migration of CO<sub>2</sub> injected at depths in excess of a 100 m to the shallow subsurface has yet to be fully quantified (Mayer et al., 2015). CO<sub>2</sub>, for example, is both highly soluble and reactive in shallow systems (e.g. Gilfillan et al., 2009) which limits the sensitivity of early seepage detection. There are many sources of DIC in subsurface waters, including the weathering of carbonate and silicate

minerals by acid rain, the breakdown of organic matter and plant respiration. Each of these processes leads to wide and overlapping  $\delta^{13}\text{C}_{\text{DIC}}$  ranges, meaning the typical range in natural subsurface waters is -5 to -25‰ (Kendall et al., 1995), which is within the range observed when fossil fuel derived  $\text{CO}_2$  equilibrates with water (Flude et al., 2016; Petroleum Technology Research Centre, 2011).

Noble gases are intimately associated with all natural and engineered  $\text{CO}_2$  occurrences, being trace components in the gas mixture in parts per billion quantities. There are three distinct sources of noble gases within the subsurface, namely the crust, the mantle and the atmosphere, and these can be discriminated and “fingerprinted” by both their isotopic compositions and abundance ratios of each isotope (Ballentine et al., 2002; Gilfillan et al., 2014; Holland and Gilfillan, 2013). Helium, in particular has proved to be effective at tracing deep input to shallow systems due to its extremely low concentration in the atmosphere of 5.2 parts per million (Torgersen et al., 1992). This low abundance allows the presence of small additional quantities of helium above the atmospheric level to be readily resolved. There are only two helium sources that result in concentrations above the atmospheric level in subsurface fluids. Helium produced through the radiogenic decay of U and Th in the crust, which yields the  $^4\text{He}$  isotope, with the other source in crustal fluids being the mantle (Ballentine and Burnard, 2002). Helium derived from the Earth’s mantle is contrastingly rich in the  $^3\text{He}$  isotope, and widely contributes to sedimentary fluids (Ballentine et al., 2002; Kennedy and van Soest, 2007; Marty et al., 1992; Oxburgh et al., 1986; Marty et al., 1993; Ballentine et al., 2002; Kennedy and van Soest, 2007). Differing helium inputs from these distinct sources results in a range of  $^3\text{He}/^4\text{He}$  ratios being observed in fluids present in almost all sedimentary basins (Ballentine et al., 2002; Castro et al., 1998).

The use of noble gases in tracing  $\text{CO}_2$  origins and its fate within natural  $\text{CO}_2$  accumulations and hydrocarbon reservoirs has been demonstrated in a number of studies (Gilfillan et al., 2008; Gilfillan et al., 2009; Györe et al., 2015; Holland and Gilfillan, 2013; Nimz and Hudson, 2005; Zhou et al., 2012). Recent work has shown that noble gases can trace  $\text{CO}_2$  dissolved in the groundwater migrating to the surface above the St. Johns Dome natural  $\text{CO}_2$  reservoir in Arizona (Gilfillan et al., 2011). The noble gas composition of shallow groundwaters and surface waters found above this natural  $\text{CO}_2$  reservoir exhibited low  $^3\text{He}/^4\text{He}$  ratios, and elevated  $^4\text{He}/^{20}\text{Ne}$  ratios, indicating a clear link to the noble gas composition measured in  $\text{CO}_2$  in the deep reservoir below (Gilfillan et al., 2011). This link has been further corroborated by recent cation and trace element analysis of springs and groundwaters in the vicinity of the St. Johns  $\text{CO}_2$  reservoir, which confirmed the presence of an additional dissolved  $\text{CO}_2$  component in the shallow groundwaters (Keating et al., 2014).

Noble gas fingerprinting techniques have also recently been used to identify micro-seepage of CO<sub>2</sub> and CH<sub>4</sub> above the Teapot Dome oil field in Wyoming (Mackintosh and Ballentine, 2012). This study found that <sup>3</sup>He/<sup>4</sup>He ratios in the soils gas were considerably below the atmospheric ratio, due to the addition of a radiogenic <sup>4</sup>He component, which was also reflected by elevated <sup>4</sup>He concentrations and <sup>4</sup>He/<sup>20</sup>Ne ratios relative to atmospheric values. Mackintosh and Ballentine (2012) concluded that the detection of crustal-sourced helium micro-seepage into water saturated systems will be enhanced by two orders of magnitude compared with soil gases. This is due to the low solubility of helium in water which results in a baseline concentration which is two orders of magnitude lower than the expected atmospheric <sup>4</sup>He concentration in a soil gas (Mackintosh and Ballentine, 2012).

Additionally, noble gases have recently proved to be effective at identifying the source of fugitive CH<sub>4</sub> contamination of groundwaters overlying the Marcellus and Barnett shale formations related to shale gas extraction (Darrah et al., 2014), and in resolving the origin of naturally elevated CH<sub>4</sub> levels of shallow groundwaters in the northern Appalachian basin (Darrah et al., 2015). These studies highlighted that groundwater wells with high CH<sub>4</sub> concentrations, located close to gas production wells, had elevated concentrations of <sup>4</sup>He and below expected concentrations of <sup>20</sup>Ne and <sup>36</sup>Ar (Darrah et al., 2014). The elevated <sup>4</sup>He concentrations were attributed to the presence of thermogenic derived CH<sub>4</sub> gas, whilst the lower than expected concentrations of <sup>20</sup>Ne and <sup>36</sup>Ar in the waters were attributed to the migrated methane gas having significantly lower <sup>20</sup>Ne and <sup>36</sup>Ar concentrations than a groundwater in contact with the atmosphere. This results in the migrating methane ‘stripping’ out the <sup>20</sup>Ne and <sup>36</sup>Ar as noble gases are more soluble in methane than in water. The process is identical to the stripping of formation waters which has been observed in natural CO<sub>2</sub> reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012) and recently in a CO<sub>2</sub>-EOR field (Györe et al., 2017; Györe et al., 2015). This noble gas stripping process provides an additional means to test for the presence of a deep subsurface sourced gas that is depleted in atmospheric noble gases.

## 2.2. Approach

We aimed to evaluate the effectiveness of  $\delta^{13}\text{C}_{\text{DIC}}$ , <sup>3</sup>He/<sup>4</sup>He, <sup>4</sup>He/<sup>20</sup>Ne, Ne, Ar and Kr fingerprints in determining the validity of the allegations of CO<sub>2</sub> leakage made on the Kerr property. To achieve this we undertook measurements of a suite of noble gases and C stable isotope tracers from three different sources: (i) CO<sub>2</sub> injected into the field (injected CO<sub>2</sub>); (ii) fluids produced from the field (produced CO<sub>2</sub>); (iii) groundwaters at the Kerr property and surrounding area (Kerr groundwaters). We aimed to determine if migration CO<sub>2</sub> originating from either the CO<sub>2</sub> injected into, or CO<sub>2</sub> contained in the fluids produced from the Weyburn

field was responsible for the alleged elevated CO<sub>2</sub> concentrations on the Kerr property. To do this we compare the noble gas and C isotope fingerprints between type (i), (ii) samples to those of type (iii), the Kerr groundwaters.

Based on the studies outlined in the Scientific Background section we hypothesise that any external CO<sub>2</sub> addition to the Kerr groundwaters, bar those of shallow subsurface biologic processes, would result in either the addition of crustal derived <sup>4</sup>He and/or a depletion in the main atmospheric derived noble gases of <sup>20</sup>Ne, <sup>36</sup>Ar, <sup>40</sup>Ar and Kr. The addition of a crustal radiogenic <sup>4</sup>He component can be identified by elevated <sup>4</sup>He/<sup>20</sup>Ne ratios above those of the atmosphere and/or a reduction in <sup>3</sup>He/<sup>4</sup>He ratios below those of atmospheric values. We focus on the Kerr groundwaters as opposed to soil gases based on the study of Mackintosh and Ballentine (2012) which showed helium anomalies would be enhanced by two orders of magnitude compared with soil gases as a result of the low solubility of helium in water.

### 3. Methods

Sample collection was undertaken over a period of three days in late June 2011, some 11 months following the soil gas sampling undertaken in the previous summer on which the leakage allegations were based (Lafleur, 2010). Samples of injected CO<sub>2</sub> were collected from a the sampling port of a Cenovus injection well (Well ID - 101/12-04-006-13 W2/0) located approximately 10 km northwest of the Kerr quarter. A sample of CO<sub>2</sub> separated from the produced reservoir fluids (produced gas, water and oil) was collected from the sampling port of the flowline emerging from a Cenovus satellite processing facility located at 16-30-05-13 (Fig. 1). This flowline contained produced gas separated by the first stage separation system at the satellite site from the oil, gas and water collected from 14 production wells that surrounded the Kerr property. Gases were collected from both the pressurised injection well and the satellite processing facility flow line using a high pressure to low pressure step down regulator, allowing gas collection at slightly above atmospheric pressure in 70 cm long vacuum tight copper tubes held in aluminium clamps. Shallow groundwaters were collected from the domestic groundwater well on the Kerr farm, two domestic groundwater wells on the adjacent Thackeray farm and the IPAC No. 1 monitoring well which was drilled during the sampling program. This was located as close to the maximum CO<sub>2</sub> anomaly reported by Petro-Find as possible given the underlying ground conditions required for the drilling rig (Lafleur, 2010) (Fig. 1). All of the wells were of standard shallow groundwater bored type construction, drilled using a rotary bucket auger and completed with PVC casing utilising a sand screen at the base. Each well was 0.762 m in diameter, ranging in depth below ground surface from 3.09 m (Thackery Farm Well) to 12.29m (Thackery House Well). Groundwater was encountered between 1.76m (IPAC ~1 monitoring well) and 3.56m below ground level. Samples were



collected from the base of the well water volumes using a peristaltic pump, with each well being pumped until water chemistry parameters established before sample collection.

$\delta^{13}\text{C}$  ( $\text{CO}_2$ ) values of the gas samples and  $\delta^{13}\text{C}_{\text{DIC}}$  values of the waters were determined at the University of Rochester using a Delta S (Finningan) mass spectrometer and the analytical error was  $\pm 0.2$  ‰. Standard extraction and purification procedures were used (Jenden et al., 1993) and the ratios are expressed as  $\delta^{13}\text{C}$  ‰ V-PDB. The dissolved gases were extracted on a stainless steel and 1720 glass extraction line at the University of Rochester using standard procedures (Poreda et al., 2004). Noble gas isotopic ratios ( $^3\text{He}/^4\text{He}$ ,  $^{20}\text{Ne}/^{22}\text{Ne}$ ,  $^{21}\text{Ne}/^{22}\text{Ne}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$ ,  $^{38}\text{Ar}/^{36}\text{Ar}$ ) and elemental abundances ( $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$  and Kr) were determined on the University of Rochester's VG 5400 mass spectrometer, using established techniques (Poreda and Farley, 1992). Bulk gases were purified by consecutive exposure to a Zr-Al getter (SAES ST-707) held at  $450^\circ\text{C}$  and a SAES SORB-AC cartridge held at  $250^\circ\text{C}$  then cooled to  $25^\circ\text{C}$ . This was followed by the sequential trapping of Ar into an activated charcoal finger at liquid  $\text{N}_2$  temperature ( $-178^\circ\text{C}$ ) and the He and Ne into an activated charcoal finger at  $-261^\circ\text{C}$ . He was released from the cryogenic finger at  $-242^\circ\text{C}$  and expanded into the spectrometer and measured, followed by Ne and Ar analyses. He, Ne, Ar, and Kr concentrations were determined by comparison to an air standard of known volume ( $0.77\text{ cm}^3$ ). Helium isotope ratios were normalized using a Rochester air standard. Neon isotope ratios were corrected for interference by measurement of  $^{40}\text{Ar}^{2+}$  and  $\text{CO}_2^{2+}$  ( $^{40}\text{Ar}^{2+}$  was typically  $< 0.4$  % of total  $^{20}\text{Ne}$  signal on the faraday cup and  $\text{CO}_2^{2+}$  was below detection limits for  $^{22}\text{Ne}$ ). The two sigma analytical error for the  $^3\text{He}/^4\text{He}$  ratio is approximately 0.5% and those for both the  $^{40}\text{Ar}/^{36}\text{Ar}$  and He/Ne isotope ratios were 0.2 %, and 0.3 % for  $^{38}\text{Ar}/^{36}\text{Ar}$  and 1 % for  $^{20}\text{Ne}/^{22}\text{Ne}$ ,  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  and 1.5 % for all noble gas abundances. Helium isotope ratios ( $^3\text{He}/^4\text{He}$ ) are expressed relative to the ratio in air ( $R_a = R_{\text{measured}} / R_{\text{air}}$  where  $R_{\text{air}} = 1.399 \times 10^{-6}$ ). All other ratios are absolute values. The majority of the duplicate sample ratios and concentrations are within 5 % of each other. Two sigma errors to the last significant figure are reported for both gas ratios and concentrations and these may be taken as limits of detection for small associated data values.

We report the concentrations of noble gases dissolved in water, rather than the concentrations of noble gases in the headspace gas degassed from the waters. This is because the amount of headspace (ie non noble gas) gases exsolved from the Kerr groundwaters was insufficient to obtain high quality ratio concentrations of noble gases relative to the total exsolved gas. However, the concentration of the individual noble gases degassed from the water samples was sufficient for high quality analysis to be performed; hence these concentrations are presented relative to the amount of water degassed. Reporting the dissolved noble gas

concentration in groundwaters in this manner is standard practice in shallow groundwaters where small quantities of dissolved gases are present (Kipfer et al., 2002).

To allow direct comparison between the different sample types, and to detect any external input to the Kerr groundwaters from the Weyburn EOR operations, we calculate the noble gas concentration in water that would arise from equilibrium of the noble gases within the injected and produced CO<sub>2</sub> with a shallow groundwater in the area surrounding the Kerr property. Using the average measured groundwater well water temperature of 14.3°C (IPAC-CO<sub>2</sub>, 2011), pressure of 0.101 MPa (1 atm) and salinity value of 0.02 Molar NaCl (equivalent to the average TDS value of 1034 mg l<sup>-1</sup>, (IPAC-CO<sub>2</sub>, 2011)) we calculate the Henry's constants using empirical equations (Crovetto et al., 1982; Smith, 1985). Under these conditions the calculated Henry's constants for He, Ne, Ar, Kr and Xe are 14.12, 11.69, 3.41, 1.80 and 1.19 GPa, respectively.

We also calculate the expected concentration and isotope ratio ranges of atmosphere-derived noble gases dissolved in the groundwater, known as air-saturated water (ASW). These concentrations and ratios were obtained using established solubility equilibrium techniques (Kipfer et al., 2002), taking the range of regional recharge conditions of 10 to 25 °C (Environment Canada), an average site altitude of 580 m and assumed an entrained excess air Ne component of between 10 to 45 %. Excess air is the term given to explain the common observation that groundwaters contain atmosphere derived noble gases in excess, resulting in dissolved noble gas concentrations which are significantly larger than the expected calculated solubility equilibrium concentrations (Kipfer et al., 2002). Excess air is measured relative to Ne concentrations and is typically in the range of 10 to 50 % (Kipfer et al., 2002). As the excess air contribution only effects the atmosphere-derived noble gases, this phenomenon will not impact on the detection of a radiogenic <sup>4</sup>He noble gas component in the groundwaters.

## **4. Results**

### **4.1. $\delta^{13}\text{C}$ (CO<sub>2</sub>) and $\delta^{13}\text{C}_{\text{DIC}}$ Values**

The measured  $\delta^{13}\text{C}$  (CO<sub>2</sub>) of the CO<sub>2</sub> injected into the Weyburn field of  $-21.2 \pm 0.2$  ‰ is similar to the average value of  $-20.4 \pm 0.3$  ‰ previously reported from analysis of 8 samples of injected CO<sub>2</sub> and 8 samples of recycled CO<sub>2</sub> from the Weyburn reservoir collected between 2000 and 2010 (Mayer et al., 2013). The measured produced CO<sub>2</sub>  $\delta^{13}\text{C}$  (CO<sub>2</sub>) duplicate values obtained in this study were  $-14.8$  and  $-12.4 \pm 0.2$  ‰ (Table 1), somewhat above the range of  $-16.5$  and  $-17.7$  ‰ observed by Mayer et al., (2013) in the final stage of their study of produced gases from the Weyburn field in late 2010. The sampled Kerr groundwaters exhibit  $\delta^{13}\text{C}_{\text{DIC}}$  values ranging from  $-13.4 \pm 0.2$  ‰ to  $-19.0 \pm 0.2$  ‰ (Table 1).

#### 4.2. Noble Gas Concentrations

$^4\text{He}$  concentrations exhibit marked distinctions depending on sample type (Fig. 2). The lowest concentration of  $41.63 \pm 0.5 \mu\text{cm}^3\text{kg}^{-1}$  is that calculated for a shallow groundwater which has equilibrated with the injected  $\text{CO}_2$  (see Methods). The groundwaters sampled from the wells on and around the Kerr property (the Kerr groundwaters) exhibit a range of  $39.2 \pm 0.6$  to  $86.9 \pm 1.3 \mu\text{cm}^3\text{kg}^{-1}$  which is almost identical to the air saturated water (ASW) concentration range of  $42.1 \pm 0.6$  to  $85.8 \pm 1.2 \mu\text{cm}^3\text{kg}^{-1}$ . This indicates that there is no presence of  $^4\text{He}$  in excess of the concentration calculated for equilibrium dissolution of atmospheric noble gases into a groundwater under the recharge conditions present at the study site (see Methods). The  $^4\text{He}$  concentration of a shallow ground water in equilibrium with the produced  $\text{CO}_2$  is two orders of magnitude higher than the values recorded from the Kerr groundwaters, ranging from  $7634 \pm 115$  to  $18313 \pm 275 \mu\text{cm}^3\text{kg}^{-1}$ .

$^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$  and Kr in the shallow subsurface are primarily derived from the atmosphere. Similar to  $^4\text{He}$ , the lowest  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ , (Fig. 3)  $^{40}\text{Ar}$  (Fig. 2) and Kr concentrations are those for a formation water in equilibrium with the injected  $\text{CO}_2$ . However, in contrast to  $^4\text{He}$ , the next lowest  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$  and Kr concentrations are those calculated for a shallow groundwater water in equilibrium with produced  $\text{CO}_2$  from the Weyburn field (Table 2). The highest noble gas concentrations are those measured in the Kerr groundwaters, which overlap with the calculated ASW range (Table 1 and Fig. 2 and 3).

#### 4.3. Noble Gas Isotope Ratios

$^4\text{He}/^{20}\text{Ne}$  ratios exhibit considerable variation depending on sample type. The lowest ratios are those observed in the Kerr groundwaters which vary from  $0.248 \pm 0.006$  to  $0.403 \pm 0.010$ , overlapping with the ASW range of  $0.288 \pm 0.007$  -  $0.325 \pm 0.01$  (Fig. 4). The injected  $\text{CO}_2$  exhibits a higher ratio of  $12.6 \pm 0.3$ , with the duplicate produced  $\text{CO}_2$  samples ranging from  $1000 \pm 21$  to  $1488 \pm 31$ , significantly above the calculated air saturated water (ASW) range (Fig. 4). The above ASW ratios of the produced  $\text{CO}_2$  indicate an excess of  $^4\text{He}$  above atmospheric levels.

$^3\text{He}/^4\text{He}$  vary considerably between the different sample types, with the lowest values of  $0.173 \pm 0.001$  and  $0.179 \pm 0.001 R_a$  (where  $R_a$  is the air  $^3\text{He}/^4\text{He}$  ratio of  $1.399 \times 10^{-6}$ ) being observed in the  $\text{CO}_2$  produced from the Weyburn field (Fig. 5). The  $\text{CO}_2$  injected into the Weyburn field has a slightly higher ratio of  $0.193 \pm 0.001 R_a$ . The range observed in the Kerr groundwaters of  $0.880 \pm 0.004$  to  $1.103 \pm 0.006 R_a$  is significantly above that of the other samples (Fig. 5).

Other noble gas ratios of the Kerr groundwaters are within the range expected for ASW; the  $^{21}\text{Ne}/^{22}\text{Ne}$  are within 2 sigma error of the ASW ratio of  $0.0290 \pm 0.003$ .  $^{40}\text{Ar}/^{36}\text{Ar}$  are also all

within error of the calculated ASW range of  $294$  to  $296 \pm 1$ . The only non-atmospheric ratios observed are  $^{20}\text{Ne}/^{22}\text{Ne}$  that range from  $9.96 \pm 0.10$  to  $10.15 \pm 0.10$ , in excess of the air ratio of  $9.80 \pm 0.08$ . The elevation of  $^{20}\text{Ne}/^{22}\text{Ne}$  is a common observation in natural groundwaters and is thought to be the result of a solubility controlled fractionation process, where  $^{20}\text{Ne}$  dissolves preferentially to  $^{22}\text{Ne}$  (Zhou et al., 2005).

## 5. Discussion

### 5.1. Comparison of results to previous measurements from the Weyburn CO<sub>2</sub>-EOR field

For logistical and budgetary reasons it was not possible to undertake sampling in the area on and surrounding the Kerr property on multiple occasions, over an extended period. Whilst this is an obvious limitation of our study, Mayer et al., (2013) have produced an extensive compilation of both  $\delta^{13}\text{C}$  (CO<sub>2</sub>) and  $\delta^{13}\text{C}$  of DIC from both injected CO<sub>2</sub> and produced fluid samples collected at the Weyburn field over a 10 year period from 2000 to 2010. Our measured  $\delta^{13}\text{C}$  (CO<sub>2</sub>) of the injected CO<sub>2</sub> of  $-21.2 \pm 0.2$  ‰ is comparable to the average value of  $-20.4 \pm 0.3$  ‰ previously reported from analysis of 8 samples of source CO<sub>2</sub> and 8 samples of injected CO<sub>2</sub> (which includes the source CO<sub>2</sub> and a small recycled component) from the Weyburn reservoir collected between 2000 and 2010 (Mayer et al., 2013). This indicates that our injected CO<sub>2</sub> sample is representative of the CO<sub>2</sub> injected into the Weyburn field over its history.

The produced CO<sub>2</sub>  $\delta^{13}\text{C}$  (CO<sub>2</sub>) duplicate values obtained in this study were  $-14.8$  and  $-12.4 \pm 0.2$  ‰ (Table 1), somewhat above the range of  $-16.5$  and  $-17.7$  ‰ observed by Mayer et al., 2013 in the final stage of their study of produced gases from the Weyburn field in late 2010. This variation can be explained by the fact that we sampled from a satellite site producing fluids from a suite of injection wells located nearest to the Kerr property which is part of flood phase 1C rather than those of phase 1A sampled by Mayer et al., (2013). Injection of CO<sub>2</sub> into the Phase 1A area of the field commenced in 2000, with injection into the Phase 1C portion of the field commencing in 2003 (Chalaturnyk and Durocher, 2005). Mayer et al., (2013) show that  $\delta^{13}\text{C}$  (CO<sub>2</sub>) values decrease from the reservoir baseline value of  $-12.7$  ‰ over time throughout their study, as more of the injected CO<sub>2</sub> reaches the production wells, and a similar evolution would be expected in the phase 1C region of the field.

Whilst it would obviously have been beneficial to undertake multiple measurements of the CO<sub>2</sub> injected into and CO<sub>2</sub> produced from the Weyburn CO<sub>2</sub>-EOR field, the above comparison shows that the samples we have collected are representative of the range of CO<sub>2</sub> injected and CO<sub>2</sub> produced from the Weyburn field since CO<sub>2</sub> injection commenced in 2000 (Mayer et al., 2013).

## 5.2. $\delta^{13}\text{C}_{\text{DIC}}$ Values

Mayer et al. (2013) found that as  $\text{CO}_2$  concentrations increased at the Weyburn production wells, the  $\delta^{13}\text{C}$   $\text{CO}_2$  values progressively approached those of the injected  $\text{CO}_2$  ( $-20.4 \pm 0.3$  ‰ from the 16 samples outlined previously). Using their measured reservoir pH values they predicted that the  $\delta^{13}\text{C}$  of DIC in equilibrium with the injected  $\text{CO}_2$  would be  $-19 \pm 2$  ‰. However, they found that their measured values approached a value of only  $-16$  ‰, indicating that there was an additional  $\text{HCO}_3^-$  source with elevated  $\delta^{13}\text{C}$  DIC values within the reservoir. Increasing concentrations of calcium and magnesium provided independent evidence that calcite and dolomite dissolution had generated additional  $\text{HCO}_3^-$ , resulting in a contribution of  $\text{HCO}_3^-$  with a  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $+3$  ‰.

Hence, the difference of  $\delta^{13}\text{C}$  of DIC (composed of DIC in isotopic equilibrium with injected  $\text{CO}_2$  and DIC derived from carbonate dissolution) and  $\delta^{13}\text{C}$  of injected  $\text{CO}_2$  was  $+4.4$  ‰. In order to allow direct comparison to the measured  $\delta^{13}\text{C}$  DIC values in the Kerr groundwaters we use this fractionation value to calculate the  $\delta^{13}\text{C}_{\text{DIC}}$  which would be produced in water in equilibrium with  $\text{CO}_2$  which has the  $\delta^{13}\text{C}$  ( $\text{CO}_2$ ) of both the injected ( $-21.2 \pm 0.2$  ‰) and produced  $\text{CO}_2$  ( $-14.8$  and  $-12.4 \pm 0.2$  ‰). Using this fractionation value we calculate a  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-16.8 \pm 0.2$  ‰ for water in contact with the injected  $\text{CO}_2$  and a  $\delta^{13}\text{C}_{\text{DIC}}$  range of  $-10.4$  to  $-8.0 \pm 0.2$  ‰ for water in contact with the produced  $\text{CO}_2$ .

The range of  $\delta^{13}\text{C}_{\text{DIC}}$  values measured in the Kerr groundwaters of  $-13.4 \pm 0.2$  ‰ to  $-19.0 \pm 0.2$  ‰, overlaps with that of water in contact with the injected  $\text{CO}_2$  and is distinct from those exhibited by water in contact with the produced  $\text{CO}_2$ . This indicates that there is a potential link between the  $\delta^{13}\text{C}_{\text{DIC}}$  values in the Kerr groundwaters and the injected  $\text{CO}_2$ . However, this is not an unequivocal link as there are multiple sources of DIC in shallow groundwaters, with each of the sources exhibiting overlapping  $\delta^{13}\text{C}_{\text{DIC}}$  ranges. This results in a typical  $\delta^{13}\text{C}_{\text{DIC}}$  range in natural subsurface waters of  $-5$  to  $-25$  ‰ (Kendall et al., 1995). Hence, natural soil processes including plant respiration, dissolution of carbonate minerals and bacterial activity could account for the range of  $-13.4 \pm 0.2$  ‰ to  $-19.0 \pm 0.2$  ‰ observed in the Kerr groundwaters (Hendry et al., 1999; Keller and Bacon, 1998; Petroleum Technology Research Centre, 2011; Romanak et al., 2014).

Mayer et al., (2015) have undertaken a comprehensive review of the usefulness of the stable isotope composition of  $\text{CO}_2$  for leakage monitoring at  $\text{CO}_2$  storage sites, which concluded that  $\delta^{13}\text{C}$  can be a useful tracer if values in the injected  $\text{CO}_2$  are distinct from those of baseline  $\delta^{13}\text{C}$  ( $\text{CO}_2$ , DIC) at the CCS site by more than  $10$  ‰. Extensive soil gas measurements were undertaken in the vicinity of the Weyburn  $\text{CO}_2$ -EOR field prior to  $\text{CO}_2$  injection commencing in 2001 and after 10 years of injection in 2011 (Beaubien et al., 2013). Beaubien et al., (2013)

found that regional  $\delta^{13}\text{C}$   $\text{CO}_2$  soil gas values ranged from -17.3 to -23.1 ‰, overlapping with the range measured on the Kerr property of -21.7 to -22.7 ‰ by Romanak et al., (2014) and the average value of the injected  $\text{CO}_2$  of  $-20.4 \pm 0.3$  ‰ as reported by Mayer et al., (2013). These studies highlight that  $\delta^{13}\text{C}$  measurements alone cannot be used as a distinctive means to determine the origin of  $\text{CO}_2$  measured on the Kerr property as also outlined by a recent signal to noise analysis (Risk et al., 2015).

### 5.3. Mixing Modelling

Noble gases offer an additional means of pinpointing gas sources, due to the distinct deep crustal origin of  $^4\text{He}$  and the atmospheric source of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$ . Our results show that all of the noble gas concentrations and isotope ratios measured in the Kerr shallow groundwater samples are within the calculated ASW ranges (the values resulting from dissolution of atmospheric noble gases into shallow groundwater), bar those of  $^{20}\text{Ne}/^{22}\text{Ne}$  and a single sample which plots below the ASW range of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  (Thackeray House Well). This observation implies that there is no additional source of noble gases to these groundwaters bar equilibration with the atmosphere. This is distinct from observations of elevated  $^4\text{He}$  concentrations and depleted  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  values in studies where deep gas migration to the shallow subsurface has been documented (Darrah et al., 2015; Darrah et al., 2014; Gilfillan et al., 2011).

However, three of the Kerr groundwater samples exhibit below ASW  $^3\text{He}/^4\text{He}$  ratios which could indicate an additional low  $^3\text{He}/^4\text{He}$  component to these waters (Mackintosh and Ballentine, 2012). In order to fully resolve the presence of any non-atmospheric contribution to these groundwater samples, we now model how  $^4\text{He}$  concentrations,  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios of ASW would evolve through mixing with either the injected or produced  $\text{CO}_2$  from the Weyburn field. As the ASW noble gas fingerprint is determined by the solubility equilibration of the noble gases in contact with the atmosphere (see Methods) under the local recharge conditions, ASW is the accepted standard for a shallow groundwater which is uncontaminated from any other inputs (Kipfer et al., 2002). Using these three end members, mixing lines for both ratio-ratio plots and ratio-element plots can be plotted using established techniques (Langmuir et al., 1978). The direct comparison of these mixing models with the Kerr groundwater noble gas composition allows resolution of the possible contribution to the waters from both the injected or produced  $\text{CO}_2$ .

### 5.4. $^3\text{He}/^4\text{He}$ ratios and $^4\text{He}$ concentrations

In Fig. 5 a plot of  $^3\text{He}/^4\text{He}$  and  $^4\text{He}$  of the Kerr groundwaters is shown. Mixing lines on the figure depict the calculated trends which would result from mixing of the  $\text{CO}_2$  injected into, and

the CO<sub>2</sub> produced from the Weyburn field with a shallow groundwater with an ASW <sup>3</sup>He/<sup>4</sup>He (1 R<sub>a</sub>) and the average ASW <sup>4</sup>He concentration. Tick marks indicate the portion of <sup>4</sup>He originating from either the CO<sub>2</sub> injected or CO<sub>2</sub> produced from the Weyburn field on the mixing lines presented. Three of the measured groundwaters contain an excess of <sup>3</sup>He relative to the predicted concentration in ASW, resulting in <sup>3</sup>He/<sup>4</sup>He ratios above the ASW ratio of 1 R<sub>a</sub>. This can be explained by the presence of <sup>3</sup>He originating from the decay of tritium which was emitted to the atmosphere as a result of nuclear weapons testing from the 1950s to 1980s (Happell, 2004). This additional <sup>3</sup>He component is variable and creates some uncertainty around the baseline <sup>3</sup>He/<sup>4</sup>He ratio of the groundwater in the region. Hence, to account for this variation we also use the higher value of 1.1 R<sub>a</sub> as a worst case scenario for assessing the portion of noble gases originating from either the CO<sub>2</sub> produced from, or injected into, the Weyburn field.

The three Kerr groundwaters with below ASW <sup>3</sup>He/<sup>4</sup>He ratios lie close to the two mixing lines plotted. The concentration of <sup>4</sup>He measured in the fluids produced from the Weyburn field is two orders of magnitude higher than the atmospheric value, as a result of crustal radiogenic contributions from interaction with the crustal fluids present in the EOR field (Fig. 5). This is reflected in the higher than ASW <sup>4</sup>He/<sup>20</sup>Ne and lower than ASW <sup>3</sup>He/<sup>4</sup>He ratios exhibited by the produced CO<sub>2</sub> gas sample (Fig. 4). Using the mixing model presented allows us to resolve that the Kerr groundwater with the lowest <sup>3</sup>He/<sup>4</sup>He could conceivably contain a maximum 0.14 % contribution to <sup>4</sup>He from the produced fluids using the best case <sup>3</sup>He/<sup>4</sup>He endmember (1 R<sub>a</sub>) or a 0.25 % contribution using the worst case <sup>3</sup>He/<sup>4</sup>He endmember (1.1 R<sub>a</sub>).

Figure 5 highlights that a 20 % contribution using the best <sup>3</sup>He/<sup>4</sup>He (1 R<sub>a</sub>) end member and a 32 % contribution in the worst case (1.1 R<sub>a</sub>) end member contribution to the Kerr groundwaters from the injected CO<sub>2</sub> could account for the lowest <sup>3</sup>He/<sup>4</sup>He ratio observed. This is a reflection of the <sup>4</sup>He concentration of the injected CO<sub>2</sub> being at the lower range of the ASW concentration expected in the shallow groundwaters recharging at the summer temperatures experienced in Saskatchewan.

#### 5.5. <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/<sup>20</sup>Ne ratios

Plots of <sup>3</sup>He/<sup>4</sup>He against <sup>4</sup>He/<sup>20</sup>Ne ratios of the Kerr groundwaters, along with measured ratios in the CO<sub>2</sub> produced and injected into the Weyburn EOR field are shown in Figure 4. Mixing lines are shown with tick marks indicating the portion originating from either the CO<sub>2</sub> injected or produced from the Weyburn EOR field. The <sup>4</sup>He/<sup>20</sup>Ne ratios measured in samples of the produced and injected CO<sub>2</sub> into the Weyburn field are above the ASW range of 0.288 ± 0.001 - 0.322 ± 0.001, and all of the Kerr groundwaters exhibit <sup>4</sup>He/<sup>20</sup>Ne ratios which are within error of the calculated ASW range (Fig. 4).

Using the mixing model presented allows determination that the Kerr groundwater with the lowest  $^3\text{He}/^4\text{He}$  and highest  $^4\text{He}/^{20}\text{Ne}$  ratios indicates a maximum of a 0.14 % contribution, in the best case scenario, to 0.25 % in a worst case scenario, to the  $^4\text{He}$  concentration from the produced  $\text{CO}_2$ . Figure 5 also shows that using the best case (1  $R_a$ ) and worst case (1.1  $R_a$ )  $^3\text{He}/^4\text{He}$  end member, a 20 % to 32 % contribution to the measured  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  of the Kerr groundwaters could originate from the  $\text{CO}_2$  injected into the Weyburn field could account for the lowest  $^3\text{He}/^4\text{He}$  and highest  $^4\text{He}/^{20}\text{Ne}$  ratio observed.

#### 5.6. $^{20}\text{Ne}$ , $^{36}\text{Ar}$ , $^{40}\text{Ar}$ , $^{84}\text{Kr}$ Concentrations

The concentrations of the noble gases heavier than He in the Kerr groundwaters are all within the expected ASW range, bar a single sample that exhibits a  $^{20}\text{Ne}$  concentration that is below the ASW range (Thackeray House Well). This is significant as the  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$  and  $^{84}\text{Kr}$  concentrations measured in the produced and injected gases and injected water are considerably lower than those in the Kerr groundwaters. Hence, if there was addition of a component of the produced or injected gases from the Weyburn field to the Kerr groundwaters it would be expected that the concentrations of  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$  and  $^{84}\text{Kr}$  would be lower than that of ASW. Whilst the Thackeray House well does exhibit a below ASW  $^{20}\text{Ne}$  concentration it also has an above ASW  $^3\text{He}/^4\text{He}$  ratio, and shows a  $^4\text{He}/^{20}\text{Ne}$  ratio which is within the ASW range. Additionally this groundwater sample does not have an elevated  $^4\text{He}$  or a depleted  $^{36}\text{Ar}$  concentration compared to the predicted ASW range.

Recent work using noble gases to investigate the contamination of groundwaters by natural gas from unconventional gas production in the USA has shown that well waters with high methane concentrations, located close to gas production wells, have below ASW concentrations of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  (Darrah et al., 2014). This is a result of the fugitive methane containing insignificant concentrations of groundwater derived  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  concentrations and consequently the migrating methane ‘strips’ out these noble gases from the groundwaters. This occurs as the noble gases are much more soluble in  $\text{CH}_4$  than in water and is identical to the stripping of formation waters which has been observed in natural  $\text{CO}_2$  reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012) and recently in a  $\text{CO}_2$ -EOR field (Györe et al., 2015). Noble gases are also considerably more soluble in  $\text{CO}_2$  than water (Warr et al., 2015) so the presence of an active flux of  $\text{CO}_2$  to the Kerr groundwaters would be expected to lower the concentration of both  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  by a similar ‘stripping’ process.

Additionally, the groundwater samples with elevated  $\text{CH}_4$  concentrations reported by Darrah et al., (2014) also exhibited above ASW  $^4\text{He}/^{20}\text{Ne}$  ratios, as a result of the presence of increased levels of radiogenic  $^4\text{He}$  which had migrated from depth (Darrah et al., 2014). A similar trend has recently been observed in naturally methane rich shallow aquifers of the



Appalachian Basin (Darrah et al., 2015). Elevated  $^4\text{He}/^{20}\text{Ne}$  ratios were also observed in all of the spring and well water samples collected from directly above the St. Johns Dome  $\text{CO}_2$  reservoir, whilst three springs located away from the reservoir had ASW  $^4\text{He}/^{20}\text{Ne}$  ratios (Gilfillan et al., 2011). The Appalachian study of the tracing fugitive  $\text{CH}_4$  contamination of groundwaters and previous noble gas measurements in both groundwaters at St. Johns (Gilfillan et al., 2011) and soil gases at Teapot Dome (Mackintosh and Ballentine, 2012) shows that  $^4\text{He}/^{20}\text{Ne}$  ratios are a sensitive tool to identify the migration of any deep gas input into the shallow subsurface. Hence, if  $\text{CO}_2$  from depth were migrating to the shallow groundwaters on the Kerr Farm, elevated  $^4\text{He}/^{20}\text{Ne}$  ratios would be expected to be observed in the groundwater samples based on these previous studies.

#### *5.7. Limitations of this study and recommendations for future application of noble gas tracers in contested situations*

The absence of elevated  $^4\text{He}/^{20}\text{Ne}$  ratios in the Kerr groundwaters corresponds to the  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  concentration measurements, showing that there is limited evidence of migration of the injected or produced  $\text{CO}_2$  from the Weyburn field into the Kerr groundwaters. However, we are unable to rule out a best case possibility of a 0.14 %, and a worst case possibility of a 0.25 %, contribution to the groundwater sample with the lowest  $^3\text{He}/^4\text{He}$  ratio from the produced fluids, or a 20 % to 32 % contribution from the injected  $\text{CO}_2$  to the sample with the lowest  $^3\text{He}/^4\text{He}$  ratio. The inability to firmly rule out a significant contribution to the Kerr groundwaters from the injected  $\text{CO}_2$  is a key limitation of our study and is due to the low helium concentrations measured in the injected  $\text{CO}_2$ . This is most likely to be the result of the solubility based capture method used to extract the  $\text{CO}_2$  from the gasification process, which results in the majority of the insoluble  $^4\text{He}$  being lost as it is not captured by the capture technique and hence is vented with the non-captured flue gas (Flude et al., 2016).

As we find no evidence of a  $^4\text{He}$  component above that of ASW we conclude that the below ASW  $^3\text{He}/^4\text{He}$  ratios are most probably the result of measured low  $^3\text{He}$  concentrations, a potential reflection of increased analytical error in measuring such small amounts of  $^3\text{He}$  in the waters. This is due to the extremely low concentration of  $^3\text{He}$  in ASW of 60 to 120 parts per trillion and highlights that  $^3\text{He}/^4\text{He}$  ratios are not a robust means to assess the presence of, or lack of presence of a radiogenic component in this study. We therefore recommend that future investigations of this type focus on  $^4\text{He}/^{20}\text{Ne}$  ratios, which is a more sensitive and robust measure of the presence of a non-atmospheric radiogenic component and also avoids the complication of elevated baseline  $^3\text{He}/^4\text{He}$  ratios due to the presence of tritium derived  $^3\text{He}$ .

Whilst we have included the injected  $\text{CO}_2$  end member to make a robust assessment of all of the possible sources of  $\text{CO}_2$  near to the Kerr Farm it is not necessarily valid. The nearest  $\text{CO}_2$

injection well to the Kerr quarter is located some 1.4 km away and CO<sub>2</sub> injection at this location ceased in 2005 (Cenovus Energy Inc., 2011). The section of the Weyburn EOR field located directly beneath the Kerr property has remained under water injection throughout extraction operations of the oil field since the 1960's (Sherk et al., 2011). Hence, we believe it to be unlikely that injected CO<sub>2</sub> could migrate over 1.5 km laterally and through ~1.5 km of overburden without encountering formation water containing an excess <sup>4</sup>He fingerprint inherited from the radiogenic decay process. Given that CO<sub>2</sub> is an excellent solvent (Warr et al., 2015) and has been shown to strip out radiogenic noble gases from formation waters (Darrah et al., 2015; Darrah et al., 2014; Gilfillan et al., 2008; Györe et al., 2015) we would expect any migrated injected CO<sub>2</sub> to obtain a radiogenic fingerprint high in <sup>4</sup>He. This would result in above atmospheric <sup>4</sup>He/<sup>20</sup>Ne and below atmospheric <sup>3</sup>He/<sup>4</sup>He ratios, similar to those of the produced CO<sub>2</sub>. We do not observe any presence of a radiogenic fingerprint in any of the Kerr groundwater samples.

In light of our findings, we recommend that further investigation into the composition of captured CO<sub>2</sub> is needed to quantify how useful noble gases will be in tracking injected CO<sub>2</sub> within CO<sub>2</sub> storage reservoirs and identifying how quickly the radiogenic fingerprint of the storage reservoir is inherited by injected CO<sub>2</sub>. We also recommend that operators of CO<sub>2</sub> injection sites establish both the geochemical baseline of their reservoir prior to CO<sub>2</sub> injection, and routinely monitor the geochemical fingerprint of the CO<sub>2</sub> injected, including both stable carbon and noble gas isotopic measurements. This comprehensive geochemical database could then be used as a robust reference basis for geochemical investigations should allegations of leakage be made.

#### *5.8. Comparison with findings from other studies completed on the Kerr site*

Our interpretation that there is no evidence of migration of the CO<sub>2</sub> injected into or produced from the Weyburn EOR field into the Kerr groundwaters is further corroborated by comparison with the results of separate investigations into the allegations of CO<sub>2</sub> contamination on the Kerr property. <sup>14</sup>C measurements were a key component of the investigation instigated by the field operators, Cenovus, by TRIUM Environmental Inc. This study analysed radiocarbon within 78 samples of soil gases over the entire of the Kerr quarter and found that these contained high levels of <sup>14</sup>C, indicating a recent carbon source. The <sup>14</sup>C values measured were identical to those measured on a control site well outside of the Cenovus CO<sub>2</sub>-EOR operations, whilst <sup>14</sup>C measurements from CO<sub>2</sub> originating from the Dakota gasification plant and the recycled gas injected into the Weyburn field showed that these contained no measurable <sup>14</sup>C (Cenovus Energy Inc., 2011). This showed that the CO<sub>2</sub> contained in the soil gases overlying

the Kerr property had to have a recent, 'living' high  $^{14}\text{C}$  source, rather than a 'dead' non  $^{14}\text{C}$  containing fossil fuel origin.

Further support to the lack of evidence of  $\text{CO}_2$  migration from depth is provided by the relationship between the concentration of  $\text{O}_2$  and  $\text{N}_2$  with  $\text{CO}_2$  in the soil gas samples in both the investigation performed on behalf of the field operators (Cenovus Energy Inc., 2011) and that performed by IPAC- $\text{CO}_2$  (Romanak et al., 2014). The Cenovus funded study found that soil gas  $\text{CO}_2$  measurements for both the Kerr Quarter and two off site control localities were in natural equilibrium with  $\text{N}_2$  and  $\text{O}_2$ , providing an indication of the origin of the  $\text{CO}_2$ . If the  $\text{CO}_2$  was from a natural biogenic soil respiration process,  $\text{O}_2$  is consumed to yield  $\text{CO}_2$  within the soil due to plant and microbial respiration activity. As a result of this consumption of  $\text{O}_2$  its concentration decreases, whilst  $\text{CO}_2$  is produced and its concentration increases.  $\text{N}_2$  concentration is unaffected in that natural process. In contrast, if the injected, industrial source  $\text{CO}_2$  was migrating to surface soils,  $\text{N}_2$  concentrations would decrease as it is displaced from the soil by the anthropogenic  $\text{CO}_2$ . No such change in  $\text{N}_2$  concentrations was observed in either the Cenovus or IPAC- $\text{CO}_2$  funded studies (Cenovus Energy Inc., 2011; Romanak et al., 2014). In addition, seasonality of soil gas  $\text{CO}_2$  concentrations was suggested in the Cenovus study as soil gas  $\text{CO}_2$  concentrations measured in September were lower than those in August. This is indicative of a natural cycle where plant and microbial based activity declines as summer ended and winter approached (Cenovus Energy Inc., 2011).

## **6. Conclusions**

We conclude that the carbon isotope data do not constrain the origin of elevated dissolved  $\text{CO}_2$  concentrations in the Kerr groundwaters, due to the lack of a distinct fingerprint between the injected and produced  $\text{CO}_2$  relative to that of baseline values in the shallow subsurface in the region. Our combined noble gas fingerprints show no evidence of the presence of noble gases from the injected  $\text{CO}_2$ , or from the  $\text{CO}_2$  produced from the Weyburn  $\text{CO}_2$  Enhanced Oil Recovery field, within the groundwaters surrounding the Kerr property. All of the Kerr groundwater samples exhibit noble gas fingerprints which would be expected in shallow groundwaters and show no evidence for the addition of a deep radiogenic component or dilution from the addition of a gas phase low in atmospheric derived noble gases.

However, we are unable to categorically rule out a best case possibility of a 0.14 %, and a worst case possibility of a 0.25 %, contribution to the groundwater sample with the lowest  $^3\text{He}/^4\text{He}$  ratio from the produced fluids, or a 20 % to 32 % contribution from the injected  $\text{CO}_2$  to this sample. The inability to firmly rule out a significant contribution to the Kerr groundwaters from the injected  $\text{CO}_2$  is a key limitation of the noble gas fingerprinting technique used in this study. This is the result of low helium concentrations measured in the injected  $\text{CO}_2$ , most

probably due to the solubility based capture method used to capture the CO<sub>2</sub>. However, we believe it is unlikely that injected CO<sub>2</sub> could migrate from the nearest CO<sub>2</sub> injection well (some 1.5 km away, and at a depth of 1.5 km) without encountering formation water rich in radiogenic noble gases and inheriting a radiogenic fingerprint high in <sup>4</sup>He and with a low <sup>3</sup>He/<sup>4</sup>He ratio, similar to that of the produced CO<sub>2</sub>.

We also determine that <sup>4</sup>He/<sup>20</sup>Ne ratios are a more robust indicator of the lack of a deep radiogenic component in the Kerr groundwaters than <sup>3</sup>He/<sup>4</sup>He ratios. This is due to a combination of the difficulties in measuring the extremely small amounts of <sup>3</sup>He present in the groundwaters and complications in determining the baseline <sup>3</sup>He/<sup>4</sup>He ratio as a result of the presence of tritogenic derived <sup>3</sup>He. Additionally, there is a significantly larger sensitivity in using <sup>4</sup>He/<sup>20</sup>Ne ratios, as opposed to <sup>3</sup>He/<sup>4</sup>He ratios, as there is a considerably larger range between deep radiogenic fluids and groundwaters in equilibration with the atmosphere (Risk et al., 2015). Hence, we recommend that future investigations of near-surface contamination by deep fluids utilising noble gases focus on <sup>4</sup>He/<sup>20</sup>Ne ratios and <sup>4</sup>He concentrations as opposed to <sup>3</sup>He/<sup>4</sup>He ratios.

Combining the conclusions of our study with the findings of the hydrological and soil gas analysis undertaken as a separate strand of the IPAC-CO<sub>2</sub> investigation, indicates the CO<sub>2</sub> found on the Kerr property is of biological origin (IPAC-CO<sub>2</sub>, 2011; Romanak et al., 2014). This corroborates the findings of the Cenovus commissioned study into the allegations, which used <sup>14</sup>C data to show that the CO<sub>2</sub> present on the Kerr property was of modern origin as opposed to the geologically old CO<sub>2</sub> injected into the Weyburn field (Cenovus Energy Inc., 2011). Hence, it is clear that the integration of the full range of geochemical tracers (stable carbon and <sup>14</sup>C isotopes, noble gases, water chemistry, process based gas ratios) is the most effective means to understand the CO<sub>2</sub> source and refute the leakage allegations made at the Kerr Farm. Therefore, future investigations into allegations of CCS related CO<sub>2</sub> leakage should use a similar comprehensive range of geochemical tools and integrate them with a good understanding of geological and engineering data at the site.

## **Acknowledgements**

We acknowledge the helpful and constructive reviews from five anonymous reviewers that commented on a previous related manuscript and two anonymous reviewers who provide constructive comment on this version. We thank Thomas Ogilvie, Dr Janis Dale and Karen Collins for help in field collection of the water samples. We further acknowledge the cooperation of Cameron and Jane Kerr along with Ian and Sheila Thackeray, property owners, Goodwater, SK, for providing access to their property and allowing us to collect water samples. We also thank Allan Greeves, of Cenovus Energy Inc., for assistance in obtaining samples

659 from Cenovus wells. This research was funded by IPAC-CO<sub>2</sub>, Scottish Carbon Capture and  
660 Storage and a NERC Postdoctoral Research Fellowship NE/G015163/1 to Stuart M.V.  
661 Gilfillan.

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## Figure Captions

**Figure 1.** Location Map (inset) showing the location of the Weyburn-Midale CO<sub>2</sub> Storage and Monitoring Project and the approximate location of the CO<sub>2</sub> pipeline which transports CO<sub>2</sub> to the field from Beulah, North Dakota after (Emberley et al., 2004). Main image is an aerial photograph showing the localities of the wells sampled in this study in relation to the town of Goodwater and the Kerr property (SW30). Grid lines indicate the UTM grid, aerial photograph courtesy of Google

**Figure 2.** <sup>4</sup>He plotted against <sup>40</sup>Ar for the Kerr groundwaters, CO<sub>2</sub> and fluids produced from the Weyburn field. <sup>4</sup>He and <sup>40</sup>Ar are both produced in the crust by radioactive decay, and so are more abundant in deep derived fluids. The Kerr groundwater samples plot within the concentrations expected in a shallow groundwater, termed air saturated water (ASW), recharging under the summer temperature conditions experienced in Saskatchewan (15 – 25 °C), including a typical excess air component of 10 - 45 %. All analytical error bars are smaller than printed symbols.

**Figure 3.** <sup>20</sup>Ne plotted against <sup>36</sup>Ar for the Kerr groundwaters, CO<sub>2</sub> injected and fluids produced from the Weyburn field. Both <sup>20</sup>Ne and <sup>36</sup>Ar in shallow groundwaters are primarily derived from the atmosphere. The Kerr groundwater samples plot within the expected concentrations in a shallow groundwater, bar one sample (Thackeray House well), which shows a slight depletion in <sup>20</sup>Ne compared to the calculated ASW range. Both <sup>20</sup>Ne and <sup>36</sup>Ar values in the produced fluids and the injected CO<sub>2</sub> are two orders of magnitude lower than those measured in the Kerr groundwaters. All analytical error bars are smaller than printed symbols.

**Figure 4.** <sup>3</sup>He/<sup>4</sup>He plotted against <sup>4</sup>He/<sup>20</sup>Ne for the Kerr groundwaters and CO<sub>2</sub> injected into the Weyburn field. Three of the groundwater samples exhibit above ASW <sup>3</sup>He/<sup>4</sup>He ratios. The <sup>4</sup>He/<sup>20</sup>Ne ratio of ASW is well constrained at 0.15 to 0.17 under the recharge conditions experienced in the summer in Saskatchewan. High <sup>20</sup>Ne content relative to <sup>4</sup>He is a strong indicator of atmospheric input. The produced CO<sub>2</sub> and injected CO<sub>2</sub> exhibit <sup>4</sup>He/<sup>20</sup>Ne well above those of ASW. All analytical error bars are smaller than printed symbols.

**Figure 5.** <sup>3</sup>He/<sup>4</sup>He plotted against <sup>4</sup>He in the injected and produced CO<sub>2</sub> from the Weyburn field and the sampled groundwaters surrounding the Kerr property. All of the shallow groundwater samples exhibit <sup>4</sup>He concentrations that are within the range expected in ASW. Mixing lines on the plot depict the trend which would result from mixing a groundwater with the best case ASW <sup>3</sup>He/<sup>4</sup>He ratio of 1 R<sub>a</sub> and the average <sup>4</sup>He concentration measured in the Kerr groundwaters, with the CO<sub>2</sub> injected into and produced from the Weyburn field. All analytical error bars are smaller than printed symbols.

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